

**CERTIFICATE**

I, Daisuke ISHII,

of Shobayashi International Patent & Trademark Office

do solemnly and sincerely declare that I am conversant with the English and Japanese languages and am a competent translator thereof, and that the attached document is, to the best of my knowledge and belief, a true and correct translation of the Japanese Patent Application No. 2003-409500 filed on December 8, 2003 in the name of PHOTORESIST COMPOSITION AND METHOD OF FORMING RESIST PATTERN.

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June 6, 2008

**Date**

## DESCRIPTION

## PHOTORESIST COMPOSITION AND METHOD OF FORMING RESIST PATTERN

## TECHNICAL FIELD

[0001]

The present invention relates to photoresist compositions utilized for forming patterns into semiconductor integrated circuits by lithography. Specifically, the present invention relates to photoresist compositions that improve resist properties such as resolution and pattern formability in fine patterning by use of  $F_2$  excimer laser beams in particular, and methods of forming resist patterns using the photoresist compositions.

## BACKGROUND ART

[0002]

As well-known in the art, in lithography processes, a photoresist layer coated on a laminated semiconductor substrate is irradiated or exposed to optical beams with shorter wave lengths through a mask corresponding to a negative or positive pattern of a semiconductor integrated circuit to be formed. The photoresist compositions, applied to the photoresist layer in the lithographic processes, are typically based on a photosensitive polymer which may be turned alkaline-insoluble (negative) or alkaline-soluble (positive) through an irradiation-induced reaction. After irradiation with patterned beams, the photoresist layer is

usually subjected to post-exposure bake (hereinafter sometimes referred to as "PEB") in order to ensure the irradiation-induced reaction. Next a developing step may remove soluble portions within the photoresist layer, thereby a layer of photoresist pattern precisely corresponding to the circuit pattern that is to be formed may be produced on the laminated semiconductor substrate. After that the patterned photoresist layer may optionally be subjected to a post bake so as to be hardened sufficiently to afford durability for the next etching step. In the etching process, the surface layer or upper layer of the laminated semiconductor substrate is dry-etched along the pattern of the photoresist layer using the photoresist layer as a mask.

[0003]

Since semiconductor integrated circuits are patterned through such processes as described above, photoresist compositions are essentially demanded with the ability to produce fine patterns, namely higher resolution. As such, a positive-type resist composition is proposed that may provide higher resolution and excellent exposure margin with respect to lithography using ArF excimer laser beams (e.g. see Patent Document 1).

[0004]

In addition, novel technologies have continuously been developed for producing still finer resist patterns. In particular, lithography using  $F_2$  excimer lasers is expected to be a next-generation technology for microfabrication below 65

nm.

[0005]

Higher resolving ability will be, of course, demanded for photoresist compositions with which next-generation F<sub>2</sub> excimer lasers are utilized as the light source. In order that the resolving ability is higher, "transparency to irradiated light" is required, so that not only the surface portion, but also the bottom portion of the photoresist layer is exposed to the patterned irradiation; thus the resist layer, including the bottom portion, can be sufficiently exposed. That is, the higher the resolving ability involved the higher the transparency of the resist layer to the wavelength of 157 nm which is the main peak of the F<sub>2</sub> excimer laser spectrum.

[0006]

Accordingly, novel polymers are currently being developed in the art to provide a photoresist composition that assures that it exhibits transparency at 157 nm of the F<sub>2</sub> excimer laser spectrum by means of introducing a fluorine (F) into the polymer, and also may provide resist properties such as alkaline-solubility which is an essential characteristic for development properties at the post-exposure stage, resolving ability on pattern transfer, and etching resistance.

[0007]

Patent Document 1: Japanese Unexamined Patent Publication (JP-A) No. 2002-341539

[0008]

The polymers, into which a fluorine (F) is being

introduced described above, are currently combined with onium salts to thereby prepare resist compositions, in which the anion of the onium salt is a fluorinated alkyl sulfonic acid ion, and the onium salt is an acid generator utilized conventionally in KrF and ArF resist compositions. Such resist compositions and the exposure thereof by use of F<sub>2</sub> excimer lasers may provide finer resist patterns; however, the configuration of the resulting resist patterns is unsatisfactory in that the top portion of the resist patterns is rounded.

[0009]

In the specification, the term "resolving ability (resolution, resolving power)" means a capacity to form fine patterns, the term "pattern configuration" refers to the configuration of the resulting patterns; thus the meanings of these terms are definitely different from each other. In order to provide a novel resist composition, both the resolving ability and the pattern configuration need to be satisfactory, and thus are essential in the development of resist compositions.

[0010]

The present invention, based on the above-mentioned example provides a novel article to form fine patterns by use of F<sub>2</sub> excimer laser beams, which had been an unachieved technology as described above. That is, it is an object of the present invention to provide a photoresist composition that has improvements in the configuration of resist patterns while

maintaining higher resolving ability, specifically, to provide a photoresist composition that has improved rectangular configuration and film reduction.

# DISCLOSURE OF THE INVENTION

[0011]

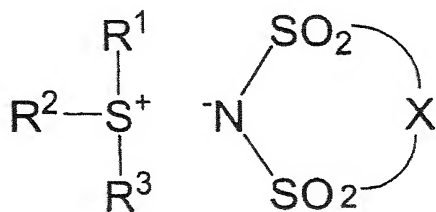
Considerable research has been carried out to solve the problem and it has been found that this can be achieved by combining a specific polymer into which a fluorine has been introduced and a specific acid generator.

[0012]

The present invention is, in the first aspect, a photoresist composition characterized in that it comprises:

(A) a polymer component comprising an alkaline-soluble constitutional unit that contains an aliphatic cyclic group having both of (i) a fluorine atom or a fluorinated alkyl group and (ii) an alcoholic hydroxide group, the alkaline solubility of the polymer component being changeable by action of an acid; and

(B) an acid generating component, capable of generating an acid by way of exposure, that contains at least a sulfonium compound expressed by the general formula (1) below:



(1)

wherein, in the formula (1), X represents a C2 to C6

alkylene group of which at least a hydrogen atom is substituted by a fluorine atom;  $R^1$  to  $R^3$  represent, independently of each other, an aryl or alkyl group; and at least one of  $R^1$  to  $R^3$  represents an aryl group.

[0013]

The present invention is, in the second aspect, a method of forming a resist pattern characterized in that it comprises coating the photoresist composition of the first aspect on to a substrate to form a resist film, selectively exposing the resist pattern, then heating and developing the resist film to thereby form a resist pattern.

[0014]

The present invention may improve defects with respect to rectangular configuration and film reduction which have been deficient in conventional photoresist compositions that contain polymers with fluorine (F) and onium salt of which the anion is a fluorinated alkyl sulfonic acid ion.

#### PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0015]

Preferred modes of the present invention will be explained in the following.

The polymer component (A), which being a base polymer of the photoresist composition according to the present invention, comprises an alkaline-soluble constitutional unit (a1) that contains an aliphatic cyclic group having both of (i) a fluorine atom or a fluorinated alkyl group and (ii) an

alcoholic hydroxide group; in which alkaline solubility of the polymer component may be changed by action of an acid. The component may be anything as long as it comprises an alkaline-soluble constitutional unit (a1) that contains an aliphatic cyclic group having both a fluorine atom or a fluorinated alkyl group (i) and an alcoholic hydroxide group (ii), and its alkaline-solubility changing by action of an acid; preferably, it is a positive-type polymer component which increases alkaline-solubility under action of an acid.

[0016]

The expression "alkaline-solubility changes by action of an acid" refers to a change of the polymer in the irradiated portion. In a case in which the alkaline-solubility increases at the irradiated portion, the polymer may be utilized as a positive-type resist since the irradiated portion turns alkaline soluble. On the other hand, in a case in which the alkaline-solubility decreases at the irradiated portion, the polymer may be utilized as a negative-type resist since the irradiated portion turns alkaline insoluble.

[0017]

The alkaline-soluble constitutional unit (a1), which contains an aliphatic cyclic group having both a fluorine atom or a fluorinated alkyl group (i) and an alcoholic hydroxide group (ii), may be anything having an aliphatic cyclic group to which is attached an organic group that contains both (i) and (ii).

[0018]



The aliphatic cyclic group may be a monocyclic or polycyclic hydrocarbon, such as cyclopentane, cyclohexane, bicycloalkane, tricycloalkane and tetracycloalkane, from which one or more hydrogen atoms are detached.

[0019]

More specifically, the polycyclic hydrocarbons may be a group of polycycloalkanes, such as adamantane, norbornane, tricyclodecane or tetracyclododecane, from which one or more hydrogen atoms are detached. Among them, the groups derived from cyclopentane, cyclohexane and norbornane, from which one or more hydrogen atoms are detached, are industrially preferable.

[0020]

The fluorine atom or fluorinated alkyl group (i) described above are a fluorine atom, or lower alkyl groups of which the hydrogen atoms are partly or entirely substituted by fluorine atoms. Specific thereof include trifluoromethyl, pentafluoroethyl, heptafluoropropyl and nonafluorobutyl groups. Among these, fluorine atoms and trifluoromethyl are industrially preferable.

[0021]

The alcoholic hydroxide group (ii) may simply be a hydroxyl group, or, alternatively, alkyloxy groups containing an alcoholic hydroxide group, alkyloxyalkyl groups containing an alcoholic hydroxide group or alkyl groups containing an alcoholic hydroxide group, for example, alkyloxy groups, alkyloxyalkyl groups or alkyl groups containing a hydroxyl

group. The alkyloxy groups, alkyloxyalkyl groups or alkyl groups may be lower alkyloxy groups, lower alkyloxyalkyl groups or lower alkyl groups respectively.

[0022]

Specific examples of the lower alkyloxy groups include methyloxy, ethyloxy, propyloxy and butyloxy groups. Specific examples of lower alkyloxyalkyl groups include methyloxymethyl, ethyloxymethyl, propyloxymethyl and butyloxymethyl groups. Specific examples of the lower alkyl groups include methyl, ethyl, propyl and butyl groups.

[0023]

The alkyloxy group containing an alcoholic hydroxide group (ii) described above may be an alkyloxy group containing an alcoholic hydroxide group, alkyloxyalkyl group containing an alcoholic hydroxide group, or alkyl group containing an alcoholic hydroxide group of which the hydrogen atoms within the alkyloxy, alkyloxyalkyl or alkyl group are partially or entirely substituted by fluorine atoms. Preferably, some portions of the hydrogen atoms within the alkyloxy moiety in the alkyloxy group containing an alcoholic hydroxide group or alkyloxyalkyl group containing an alcoholic hydroxide group are substituted by fluorine atoms. Preferably, a portion some of the hydrogen atoms within the alkyl group in the alkyl group containing an alcoholic hydroxide group are substituted by fluorine atoms, thus to form a fluoroalkyloxy group containing an alcoholic hydroxide group, fluoroalkyloxyalkyl group containing an alcoholic hydroxide group, or fluoroalkyl

group containing an alcoholic hydroxide group.

[0024]

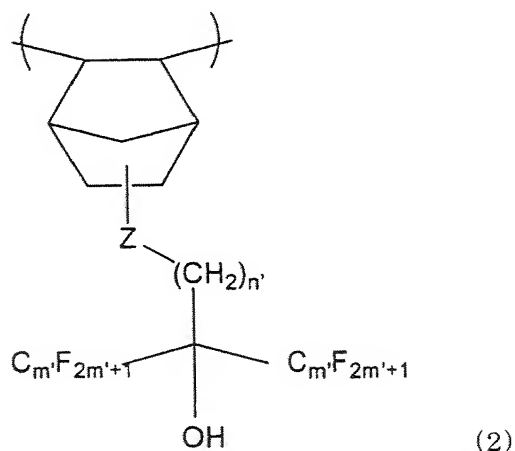
Examples of fluoroalkyloxy groups containing an alcoholic hydroxide group include  $(\text{HO})\text{C}(\text{CF}_3)_2\text{CH}_2\text{O}-$  group, 2-bis(trifluoromethyl)-2-hydroxy-ethyloxy group,  $(\text{HO})\text{C}(\text{CF}_3)_2\text{CH}_2\text{CH}_2\text{O}-$  group, 3-bis(trifluoromethyl)-3-hydroxy-propyloxy group and the like. Examples of fluoroalkyloxyalkyl groups containing an alcoholic hydroxide group include  $(\text{HO})\text{C}(\text{CF}_3)_2\text{CH}_2\text{O}-\text{CH}_2-$  group,  $(\text{HO})\text{C}(\text{CF}_3)_2\text{CH}_2\text{CH}_2\text{O}-\text{CH}_2-$  group and the like. Examples of fluoroalkyl groups containing an alcoholic hydroxide group include  $(\text{HO})\text{C}(\text{CF}_3)_2\text{CH}_2-$  group, 2-bis(trifluoromethyl)-2-hydroxy-ethyl group,  $(\text{HO})\text{C}(\text{CF}_3)_2\text{CH}_2\text{CH}_2-$  group, 3-bis(trifluoromethyl)-3-hydroxy-propyl group and the like.

[0025]

The groups (i) and (ii) perform well as long as they attach directly to the aliphatic cyclic rings. When the constitutional unit (a1) forms a unit expressed by the general formula (2) below, specifically when a fluoroalkyloxy group containing an alcoholic hydroxide group, fluoroalkyloxyalkyl group containing an alcoholic hydroxide group, or fluoroalkyl group containing an alcoholic hydroxide group is attached to a norbornene ring, then the double bond of the norbornene ring is cleaved to form a unit represented by the general formula (2) shown below, the transparency, alkaline-solubility, and dry-etching resistance are superior, and also such a constitutional unit is preferred from the viewpoint of

industrial availability.

[0026]



[0027]

In the general formula (2), Z represents an oxygen atom, oxymethylene group ( $-\text{O}(\text{CH}_2)-$ ), or single bond;  $n'$  and  $m'$  represent independently of each other an integer of 1 to 5.

[0028]

The polymer unit, utilized together with the unit (a1), may be selected from conventional ones without limitation. When it is utilized as a polymer (A-1) of which the alkaline-solubility increases by action of a positive-type acid, the constitutional unit (a2) derived from a (meth)acrylic ester having a conventional acid-dissociative dissolution-controlling group is preferable in light of higher resolving ability.

[0029]

The constitutional unit (a2) are those derived from tert-alkylesters of (meth)acrylic acids such as tert-butyl(meth)acrylate and tert-amyl(meth)acrylate.

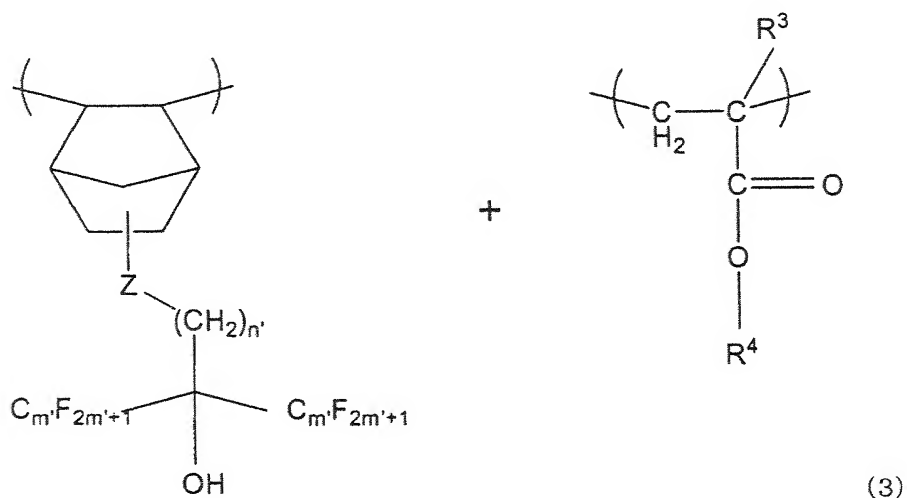
[0030]

The polymer (A) according to the present invention may be the polymer (A-2) which comprises a fluorinated alkylene constitutional unit (a3) for increasing the polymer transparency and in which alkaline-solubility increases under action of an acid. The inclusion of the constitutional unit (a3) may further increase the transparency. Preferably, the constitutional unit (a3) is one derived from tetrafluoroethylene.

[0031]

In the following, general formulas (3) and (4) are shown that represent the polymer (A-1) and (A-2) respectively.

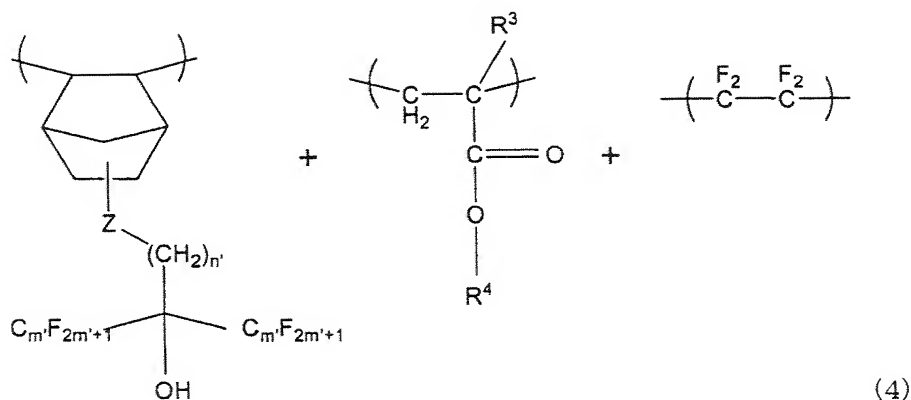
[0032]



[0033]

In the general formula (3), Z, n', and m' are as defined in the above general formula (2); R<sup>3</sup> represents a hydrogen atom or a methyl group; and R<sup>4</sup> represents an acid-dissociative dissolution-inhibiting group.

[0034]



[0035]

The meanings of Z, n', m', R<sup>3</sup> and R<sup>4</sup> in the formula (4) are the same as those in the formula (3).

[0036]

The polymer component (A-1) and the polymer component (A-2) are expressed by different formulas which include a general formula (2) respectively; however, the polymer component (A-1) and the polymer component (A-2) may be summarized into a concept of polymer components that comprise an alkaline-soluble constitutional unit (a1) that contains an aliphatic cyclic group having (i) a fluorine atom or a fluorinated alkyl group and (ii) an alcoholic hydroxide group, and the alkaline-solubility changes by action of an acid. The polymer components may also have a constitutional unit as shown below.

[0037]

That is, in the constitutional unit (a1), the fluorine atom or fluorinated alkyl group (i) and the alcoholic hydroxide group (ii) are attached to the aliphatic ring, and the cyclic group thereby constitutes the principal chain.

[0038]

The fluorine atom or fluorinated alkyl group (i) may be the same as described above, and the alcoholic hydroxide group (ii) may be simply a hydroxyl group.

[0039]

The polymer (A) having such a unit may be formed by cyclic polymerization of a diene compound having a hydroxyl group and a fluorine atom. Preferably, the diene compound is heptadiene which easily yields 5- or 6-membered ring polymers which may be excellent in transparency and dry-etching resistant; most preferably from industrial viewpoints, the polymer component is one formed via cyclic polymerization of 1,1,2,3,3-pentafluoro-4-trifluoromethyl-4-hydroxy-1,6-heptadiene ( $\text{CF}_2=\text{CFCF}_2\text{C}(\text{CF}_3)(\text{OH})\text{CH}_2\text{CH}=\text{CH}_2$ ).

[0040]

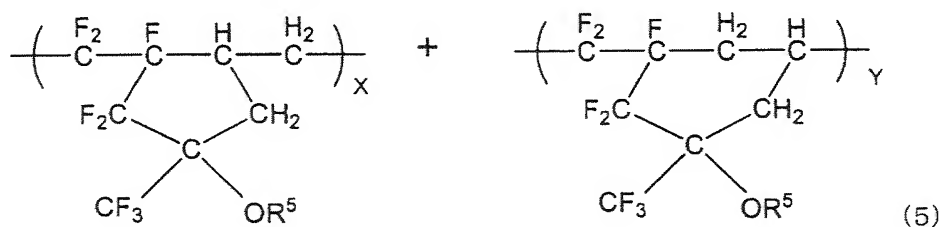
When used as a positive polymer (A-3) alkaline solubility of which increases by an action of an acid, a polymer component is preferable that contains a constitutional unit (a4) in which the hydrogen atom of the alcoholic hydroxyl group is substituted with an acid-dissociative dissolution-inhibiting group. The acid-dissociative dissolution-inhibiting group is preferably a linear, branched or cyclic alkyloxymethyl group having 1 to 15 carbon atoms from the viewpoint of proper acid-dissociative property; in particular, lower alkoxyethyl groups such as a methoxyethyl group are preferable from the viewpoint of higher resolving ability and superior pattern configuration. The rate of the acid-dissociative dissolution-inhibiting group is 10 to 40%, and

preferably 15 to 30% based on entire hydroxyl groups from the viewpoint of excellent pattern-forming ability.

[0041]

General formula (5) that expresses the polymer (A-3) is shown below.

[0042]



[0043]

In the general formula (5),  $\text{R}^5$  represents a hydrogen atom or C1 to C15 alkyloxymethyl group; preferably,  $\text{R}^5$  is a methoxymethyl group. X and Y represent mole% of 10 to 50%. A mixture of resins having different ratios in terms of protecting hydrogen atoms on the alcoholic hydroxyl group may be utilized.

[0044]

Polymer (A) as described above may be synthesized using a conventional method. The weight average molecular weight of the resin in the component (A) is, but not limited to, 5,000 to 80,000, and more preferably 8,000 to 50,000 based on polystyrene standard by way of GPC.

[0045]

The component (A) may be formed of one or more resins. Specifically, two or more components selected from (A-1), (A-2), and (A-3) described above may be blended and utilized. The

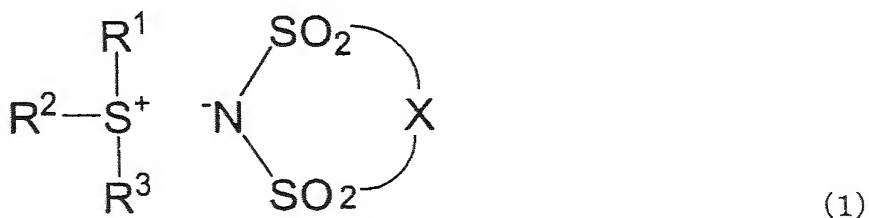


other resins selected from conventional resins for photoresist compositions may be blended and utilized in addition.

[0046]

The present invention is characterized in that the component (B) contains a sulfonium compound expressed by the general formula (1) shown below (hereinafter may be referred to as "sulfonium compound 1").

[0047]



[0048]

In the general formula (1), X represents a linear or branched alkylene group of which at least a hydrogen atom is substituted by a fluorine atom. The carbon number of the alkylene group is 2 to 6, preferably 3 to 5, and most preferably 3. With a smaller the carbon number of the alkylene group X, the solubility into the resist solvent is higher, and thus is more preferable.

[0049]

In addition, the higher the number of hydrogen atoms substituted by fluorine atoms in the alkylene group X, the higher the acid strength and this is more preferable since the transparency increases with respect to higher energy irradiation with no more than a 200 nm wavelength or electron beam. The proportion of fluorine atoms in the alkylene or

alkyl group, i.e. fluorine content, is preferably 70 to 100%, and more preferably 90 to 100%; most preferably, all of the hydrogen atoms are substituted by fluorine atoms to form a perfluoroalkylene or perfluoroalkyl group.

[0050]

$R^1$  to  $R^3$  in the general formula (1) represent, independently of each other, an aryl or alkyl group. At least one of  $R^1$  to  $R^3$  is an aryl group. Preferably, two or more of  $R^1$  to  $R^3$  are aryl groups; most preferably, all of  $R^1$  to  $R^3$  are aryl groups. The aryl group of  $R^1$  to  $R^3$  may be, for example, selected from aryl groups having a carbon number of 6 to 20 without any particular limitation, more specifically, from phenyl and naphthyl groups which may be substituted or unsubstituted by an alkyl or halogen atom. From the viewpoint of inexpensive production cost preferably,  $R^1$  to  $R^3$  are aryl groups having a carbon number of 6 to 10.

[0051]

The alkyl groups of  $R^1$  to  $R^3$  may be selected, for example, from linear, branched or cyclic alkylene groups having a carbon number of 1 to 10 without any particular limitation; preferably, the carbon number is 1 to 5 from the viewpoint of superior resolving ability. Specific examples thereof include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, cyclopentyl, hexyl, cyclohexyl, nonyl and dacyl groups. Among these, methyl groups is preferable from the viewpoint of higher resolving ability and inexpensive production cost. Most preferably, all of  $R^1$  to  $R^3$  are all

phenyl groups.

[0052]

In the present invention, the component (B) essentially contains sulfonium compound 1 in order to provide higher resolving ability and superior pattern configuration and to suppress film reduction. The sulfonium compound 1 incorporated into the component (B) may be one or more compounds.

[0053]

The total content of the compound selected from sulfonium compounds 1 is preferably 25 to 100% by mass, more preferably 30 to 100% by mass based on the entire mass of the component (B). A content of no less than 25% by mass may bring about sufficient effects of the present invention.

[0054]

In the present invention, the component (B) may contain well known acid generator utilized in chemically amplified resists.

Conventional, various acid generators exist, such as onium salts including iodonium salts and sulfonium salts, oxime sulfonates, bisalkyl or bisaryl sulfonyldiazomethanes, nitrobenzylsulfonates, iminosulfonates and disulfones. The acid generator in the component (B) may be selected from these conventional ones without particular any limitation. Among these, onium salts that contain a fluorinated alkylsulfonic acid ion as its anion (hereinafter referred to as "onium salt-type acid generator") are preferred since the strength of the generating acid is higher in general. Preferable examples of

cations of an onium salt-type acid generator are mono- or diphenyliodonium, mono-, di- or tri-phenylsulfonium, and dimethyl(4-hydroxynaphthyl)sulfonium, which may be substituted by a lower alkyl group such as methyl, ethyl, propyl, n-butyl, and tert-butyl groups or by lower alkoxy groups such as methoxy and ethoxy groups.

[0055]

Preferably, from the viewpoint of safety in handling, the anion of the onium salt-type acid generator is a fluorinated alkylsulfonic acid ion of which the alkyl group is linear and its carbon number is 1 to 7, preferably 1 to 3, and its hydrogen atoms are partly or entirely substituted by fluorine atoms. A carbon number of 7 or less may result in higher acid strength as a sulfonic acid.

[0056]

The fluorinated rate in the fluorinated alkylsulfonic acid ion (content of fluorine atoms in the alkyl group) is preferably 10 to 100%, more preferably 50 to 100%. In particular, alkyl groups of which the hydrogen atoms are entirely substituted by fluorine atoms are preferable from the viewpoint of higher acid strength. Specific examples thereof include trifluoromethane sulfonate and heptafluoropropane sulfonate.

[0057]

Specific examples of the onium salt-type acid generator include: trifluoromethanesulfonate or nonafluorobutanesulfonate of diphenyliodonium;

trifluoromethanesulfonate or nonafluorobutanesulfonate of bis(4-tert-butylphenyl)iodonium;  
trifluoromethanesulfonate, heptafluoropropanesulfonate or nonafluorobutanesulfonate of triphenylsulfonium;  
trifluoromethanesulfonate, heptafluoropropanesulfonate or nonafluorobutanesulfonate of tri(4-methylphenyl)sulfonium;  
trifluoromethanesulfonate, heptafluoropropanesulfonate or nonafluorobutanesulfonate of dimethyl(4-hydroxynaphtyl)sulfonium; trifluoromethanesulfonate, heptafluoropropanesulfonate or nonafluorobutanesulfonate of monophenyldimethylsulfonium; trifluoromethanesulfonate, heptafluoropropanesulfonate or nonafluorobutanesulfonate of diphenylmonomethylsulfonium, and the like. These onium salt-type acid generators may be used alone or in combination.

[0058]

When the onium salt-type acid generator is used in combination with at least one selected from sulfonium compounds 1 and utilized as the component (B), the content of the onium salt-type acid generator is preferably 10 to 75% by mass, and more preferably 30 to 70% by mass based on the total mass of the component (B). The onium salt-type acid generator included in the above range may suppress line edge roughness (LER) and development defects. The mixing ratio by mass of (onium salt-type acid generator):(at least one selected from sulfonium compounds) is 1:9 to 9:1, preferably 1:5 to 5:1, and most preferably 1:2 to 2:1. By using the acid generator as a mixture at the above ratio, LER and development defects may be

also suppressed. Furthermore, the term "LER" refers to non-uniform irregularities that are formed after development in resist patterns, for example, in sidewalls of a line and space pattern.

[0059]

The component (B) is employed at an amount of 0.1 to 30 parts by mass, more preferably 0.5 to 20 parts by mass, and still more preferably 1 to 10 parts by mass based on 100 parts by mass of the component (A). An amount below the lower limit may fail to form images; on the other hand, An amount above 30 parts by mass may lead to a nonhomogeneous solution, thus possibly resulting in poor preservation stability.

[0060]

The positive-type resist composition according to the present invention may be prepared via dissolving the materials into an organic solvent (C) (hereinafter referred to as "component (C)"). The component (C) may be anything or any solvent that can dissolve the respective ingredients to form a uniform solution, and conventionally, may be any one or more solvents that are selected from a group of known solvents and utilized as solvents for chemically amplified resists.

[0061]

Specific examples thereof include ketones such as gamma-butyrolactone, acetone, methylethylketone, cyclohexanone, methylisoamylketone and 2-heptanone; polyalcohols such as ethylene glycol, ethylene glycol monoacetate, diethylene glycol, diethylene glycol monoacetate, propylene glycol,

propylene glycol monoacetate and dipropylene glycol, and derivatives thereof such as of monomethylether, monoethylether, monopropylether, monobutylether and monophenylether; cyclic ethers such as dioxane; and esters such as methyl lactate, ethyl lactate, methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, ethyl pyruvate, methyl methoxypropionate and ethyl ethoxypropionate. These organic solvents may be used alone or in combination.

[0062]

There is no set limit on the amount of solvent used; the amount is adjusted so as to make it possible to coat the resist composition onto substrates and the like; in general, the solid content of the resist composition is 2 to 20% by mass, preferably 5 to 15% by mass.

[0063]

In order to enhance post exposure stability of latent images formed by pattern wise exposure of resist layers, a nitrogen-containing organic compound (hereinafter referred to as component (D)) may be optionally incorporated into the positive-type resist compositions according to the present invention. The component (D) may be selected from various compounds proposed in the art, preferably amines, in particular secondary aliphatic amines or tertiary aliphatic amines.

[0064]

The aliphatic amines refer to amines of alkyl or alkylalcohol having a carbon number of 15 or less; examples of

the secondary or tertiary amines include trimethylamine, diethylamine, triethylamine, di-n-propylamine, tri-n-propylamine, tripentylamine, trihexylamine, triheptylamine, trioctylamine, tridecanylamine, tridodecylamine, tritetradecanylamine, diethanolamine, triethanolamine, and triisopropanolamine; in particular, tertiary alkanolamine such as triethanolamine and triisopropanolamine are preferable. These may be used alone or in combination. The component (D) is used in an amount of 0.01 to 5.0 parts by mass, for 100 parts by mass of the component (A).

[0065]

In order to prevent sensitivity degradation due to the component (D), to improve configuration of resist patterns, and to enhance post exposure stability of latent images formed by pattern wise exposure of resist layers, an organic carboxylic acid or phosphorous oxo acid or derivative thereof (E) (hereinafter referred to as component (E)) may be additionally incorporated as an optional component. Furthermore components (D) and (E) may be utilized alone or in combination.

[0066]

Preferable examples of organic carboxylic acids include malonic acid, citric acid, malic acid, succinic acid, benzoic acid and salicylic acid.

[0067]

The phosphorous oxo acid or derivative thereof may be phosphoric acid and its derivatives, e.g. esters such as



phosphoric acid, di-n-butylphosphate and diphenylphosphate; phosphonic acid and its derivatives, e.g. esters such as phosphonic acid, dimethylphosphonate, di-n-butylphosphonate, phenylphosphonic acid, diphenylphosphonate and dibenzylphosphonate; phosphinic acid and its derivatives, e.g. esters such as phosphinic acid and phenylphosphinate. Among these, salicylic acid and phenylphosphonic acid are preferable in particular.

[0068]

The component (E) is utilized at a proportion of 0.01 to 5.0 parts by mass, for 100 parts by mass of component (A).

[0069]

In addition, a dissolution-controlling agent may be incorporated. Specifically, such compounds may be exemplified by lower molecular weight phenol, alcohol or carboxylic acid compounds preferably having a molecular weight of 100 to 500, in which at least one fluorine atom is attached to the compound and its solubility in alkaline developer increases by action of an acid, or alternatively a portion of hydrogen atoms of hydroxyl groups within the phenol, alcohol or carboxylic acid compounds is substituted by an acid-unstable substituent capable of controlling alkaline-solubility (acid-dissociative dissolution-controlling group).

[0070]

Examples of the acid-dissociative substituents include tertiary alkyl, tertiary alkoxycarbonyl, tertiary alkoxycarbonylalkyl, and chain or cyclic alkoxyalkyl groups.

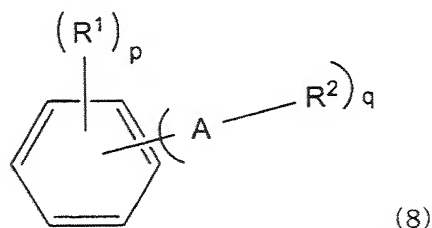
[0071]

Specific examples thereof include tertiary alkyl groups such as tert-butyl group; tertiary alkoxy carbonyl groups such as tert-butoxycarbonyl group; tertiary alkoxy carbonyl alkyl groups; chain, branched or cyclic alkyloxymethyl groups having a carbon number of 1 to 15 such as methoxymethyl, tert-amyloxymethyl and 4-tert-butyl-cyclohexyloxymethyl groups.

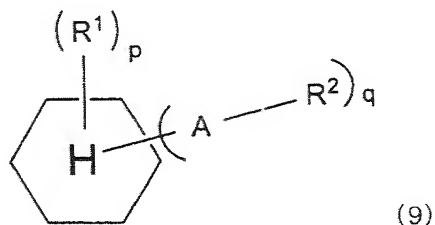
[0072]

Such compounds may be expressed by the general formulas (8) and (9), for example.

[0073]



[0074]



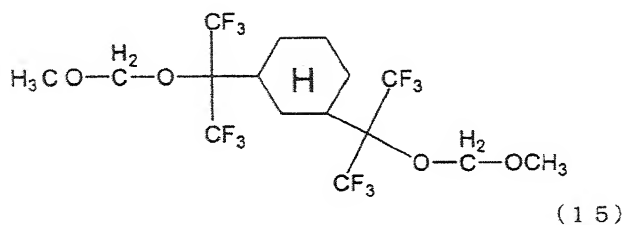
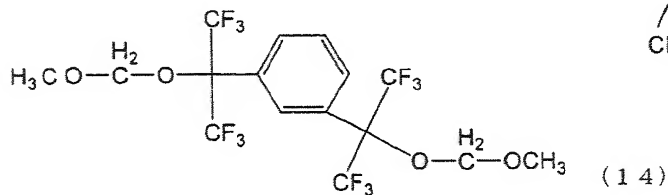
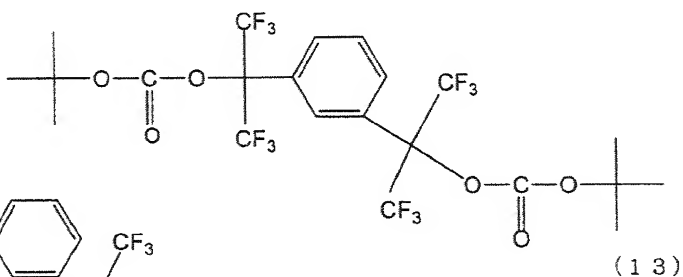
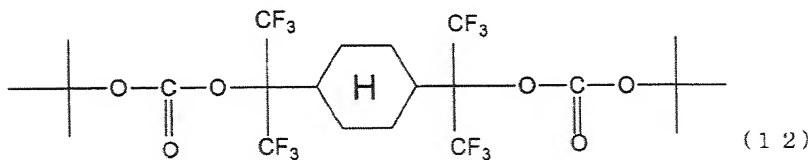
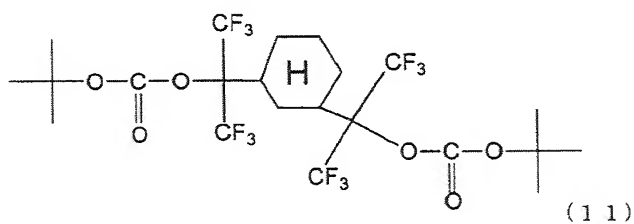
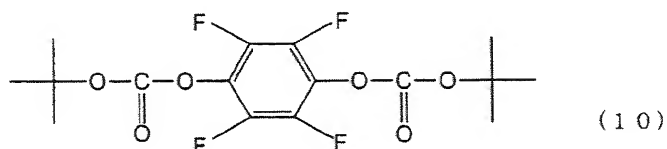
[0075]

$R^1$  represents a hydrogen atom, alkyl group, alkoxy group or fluorine atom;  $R^2$  represents an acid-dissociative dissolution-controlling group; A is  $-C(C_nF_{2n+1})-$ ,  $-(C_mF_{2m+1})-O-CO-O-$ ,  $-(C_mF_{2m+1})-O-$ , or  $-O-CO-O-$ ; n, m, p and q are independent of each other and are integers of 1 to 4, with a proviso that  $R^1$  is a fluorine atom when A is  $-O-CO-O-$ .

[0076]

More specific examples of compounds expressed by these formulas may be the compounds expressed by the chemical formulas (10) to (15) below.

[0077]



[0078]

The other compounds include 3,3',5,5'-tetrafluoro[(1,1'-biphenyl)-4,4'-di-t-butoxycarbonyl], 4,4'-[2,2,2-trifluoro-1-

(trifluoromethyl)ethylidene]bisphenol-4,4'-di-t-butoxycarbonyl, 2-trifluoromethylbenzenecarboxylic acid 1,1-t-butylester, and 2-trifluoromethylcyclohexane carboxylic acid-t-butylester.

[0079]

Among these, the compounds expressed by the chemical formulas (10) to (15) are preferable since they provide higher transparency and superior rectangular shape in fine patterns.

[0080]

Preferably, the acid-dissociative dissolution-controlling group  $R^2$  is a chain, linear or cyclic alkyloxymethyl or tertiary alkyl group having a carbon number of 1 to 15. Among others,  $R^2$  is preferably the compounds expressed by the chemical formulas (13) or (14).

[0081]

The amount of the dissolution-controlling agent in the photoresist composition according to the present invention is 2 to 30 parts by weight, and preferably 3 to 10 parts by weight for 100 parts by weight of the main component polymer (A). When the amount is less than 2 parts by weight, the dissolution-controlling effect is minor, and when the amount is above 30 parts by weight, the thermal resistance of the resist is likely to be insufficient.

[0082]

When a fluorine atom is incorporated into the dissolution-controlling agent, transparency for 157 nm wavelength light is significantly enhanced and resolving ability is improved.

[0083]

The photoresist composition according to the present invention may further contain miscible additives such as additional resins to improve the properties of resist films, surfactants to upgrade the coating properties, and dissolution-controlling agents, plasticizers, stabilizers, colorants, halation-inhibiting agents and the like if desired.

[0084]

The method of forming resist patterns according to the present invention may be carried out by forming resist patterns through a conventional lithography process using the photoresist composition described above. In the method, the photoresist composition is coated on to a substrate, for example, by way of rotary coating, and then dried to form a resist film. Then the resist film is selectively exposed through a mask pattern and then heated after the exposure. Finally, the film is developed using an alkaline solution to form a resist pattern, and then is subjected to post baking if necessary. The irradiation source is preferably  $F_2$  excimer laser beams.

[0085]

Various substrates such as organic or inorganic anti-reflective films,  $SiON$ ,  $SiN$ ,  $Si_3N_4$  and the like, having various films thereon, may be utilized as the substrate. The wavelength of the irradiation beam is not particularly limited; the irradiation source may be  $ArF$  excimer lasers,  $KrF$  excimer lasers,  $F_2$  excimer lasers, EUV (extreme ultraviolet),

VUV (vacuum ultraviolet), EB (electron beam), X-ray, soft X-ray, and the like. The resist compositions according to the present invention may be effectively employed together with F<sub>2</sub> excimer lasers.

#### Examples

[0086]

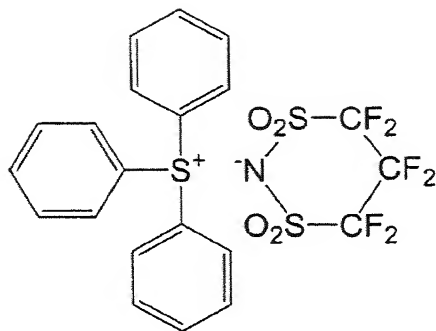
Below, the present invention will be explained in detail by way of examples, which are merely for properly illustrating the invention, and do not limit the present invention in any way.

[0087]

#### Example 1

100 parts of the fluorine-containing polymer (expressed by the previously described general formula (5), with 20% of R<sup>5</sup> being protected by a methoxymethyl group, and X:Y = 50:50 in mole ratio), 5 parts by weight of the acid generator expressed by the general formula (16) below, 0.1 parts by weight of triethanolamine, and 0.1 parts by weight of salicylic acid were added into and mixed together with 1300 parts by weight of propyleneglycol monomethylether acetate to prepare a photoresist composition.

[0088]



(16)

[0089]

A silicon wafer having a SiON thin film was employed as a substrate on which a resist film was formed. The photoresist composition described above was coated on to the substrate uniformly by spin coating, and then heated to dry at 90 degrees C for 90 seconds, to thereby prepare a resist film 180 nm thick.

[0090]

The resist film was exposed selectively through a mask by F<sub>2</sub> excimer lasers (157 nm wavelength) using F<sub>2</sub> excimer lasers irradiation system (by Exitech Co., NA=0.85, 1/2 zone).

[0091]

After the selective exposure, the resist film was heated at 120 degrees C for 90 seconds, then was developed in a solution containing 2.38% by weight of tetramethylammonium hydroxide; the developing temperature was 23 degrees C and the developing period was 60 seconds. After development, the specimen was rinsed with de-ionized water and dried.

[0092]

Observation by use of a scanning electron microscope (SEM) confirmed that a line and space (1:1.5) in 200 nm pitch

(line: 80 nm, space: 120 nm) was formed on the substrate. The sensitivity at that time was  $24.6 \text{ mJ/cm}^2$ . From the observation of the cross-section configuration, the line of the pattern clearly exhibited a rectangular shape, and no film reduction was observed.

[0093]

#### Comparative Example 1

A pattern was formed in the same manner as Example 1, except that 5.0 parts by mass of triphenylsulfonium-nonafluorobutane-sulfonate was used in place of the acid generator expressed by the formula (16) shown above.

[0094]

Observation by use of a scanning electron microscope (SEM) showed that a pattern was formed on the substrate with line and space (1:1.5) of 200 nm pitch (line: 80 nm, space: 120 nm), the top of the resist pattern was rounded, and the film reduction appeared. The sensitivity at that time was  $12.0 \text{ mJ/cm}^2$ .

#### INDUSTRIAL APPLICABILITY

[0095]

As explained above, the photoresist compositions and the methods of forming a resist pattern according to the present invention are available for patterning of semiconductor integrated circuits by lithography, and in particular are effective for fine patterning by use of  $F_2$  excimer laser beams.

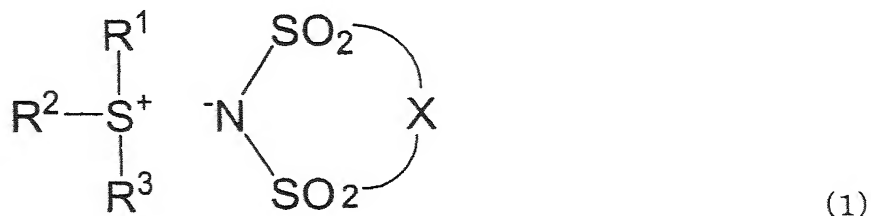


## CLAIMS

1. A photoresist composition comprising:

(A) a polymer component comprising an alkaline-soluble constitutional unit that contains an aliphatic cyclic group having both (i) a fluorine atom or a fluorinated alkyl group and (ii) an alcoholic hydroxide group, the alkaline solubility of the polymer component being changeable by action of an acid; and

(B) an acid generating component, capable of generating an acid by way of exposure, that contains at least a sulfonium compound expressed by the general formula (1) below:



wherein, in the formula (1), X represents a C2 to C6 alkylene group of which at least a hydrogen atom is substituted by fluorine atom;  $\text{R}^1$  to  $\text{R}^3$  represent, independently of each other, an aryl or alkyl group; and at least one of  $\text{R}^1$  to  $\text{R}^3$  represents an aryl group.

2. A photoresist composition according to claim 1, further comprising a nitrogen-containing organic compound.

3. A photoresist composition according to claims 1 or 2, further comprising an organic carboxylic acid, or a

phosphorous oxo acid or derivative thereof.

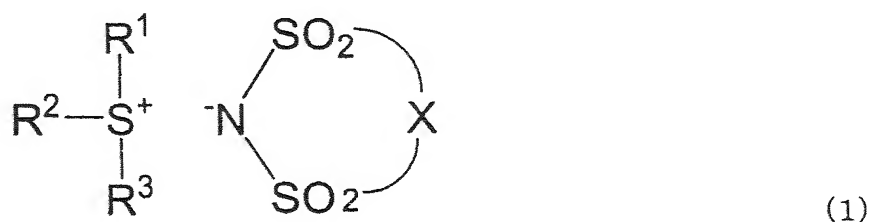
4. A method of forming a resist pattern, comprising:

coating the photoresist composition any one of claims 1 to 3 on a substrate to form a resist film,  
selectively exposing the resist film, and  
heating and developing the resist film after exposure to form a resist pattern.

5. A method of forming a resist pattern according to claim 4, wherein a SiON film is provided on the substrate.

## ABSTRACT

A photoresist composition which improves resist pattern configuration, i.e., rectangular configuration, and suppresses film reduction is provided while maintaining the resolution. A photoresist composition including: (A) a polymer component which includes an alkaline-soluble constitutional unit that contains an aliphatic cyclic group having both (i) a fluorine atom or a fluorinated alkyl group and (ii) an alcoholic hydroxyl group, and alkaline solubility of which varies with an action of an acid; and (B) an acid generating component that generates an acid by way of exposure, and that contains at least a sulfonium compound expressed by the general formula (1) below;



wherein, X represents a C2 to C6 alkylene group having substitution of at least one hydrogen atom with a fluorine atom; R<sup>1</sup> to R<sup>3</sup> each independently represent an aryl group or an alkyl group; and at least one of R<sup>1</sup> to R<sup>3</sup> represents an aryl group.